Carbon isotope variations on ancient carbonate platforms:
The roles of organic carbon burial and sea level

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Abstract

Positive $\delta^{13}C$ trends in ancient carbonate rocks are commonly interpreted to reflect increases in the burial of organic carbon in sediments. An alternative model to explain positive $\delta^{13}C$ trends in shelf carbonate rocks is related to mixing with open ocean water during transgression that floods the carbonate platform. Rock samples from two age-correlated, stratigraphic sections from the Arbuckle Mountains, Oklahoma and Clear Spring, Maryland of Middle to Upper Ordovician age were measured and sampled for $\delta^{13}C$ and $\delta^{18}O$. The $\delta^{13}C$ curves reveal 3-4 per mil positive shifts in the upper Darriwilian to lower Sandbian stages (*C. sweeti* to *gerdae* conodont zones). Lithological analysis indicates transgressive events (shallow to deeper marine) associated with the positive $\delta^{13}C$ shifts in the Appalachian foreland basin but indicates a transgressive-regressive sequence in the upper portions of the Arbuckle Mountains. Plots of $\delta^{13}C$ versus $\delta^{18}O$ reveal minimal covariance, potentially invalidating diagenetic explanations for the trend. Because $\delta^{13}C$ does not show an obvious correlation with water depth or diagenesis, these results suggest that the positive $\delta^{13}C$ positive trends of both sections may be closely related to global changes in organic carbon burial.

Introduction

  Geochemical properties of carbonate rocks have long been utilized to reconstruct various aspects of ancient ocean chemistry and climate. In particular, isotopic indicators, such as $\delta^{13}C$ and $\delta^{18}O$ from carbonate, are commonly interpreted as proxies for changes in carbon dioxide and temperature, respectively, throughout geologic time. The interpretations for these isotopic indicators hinge on the assumption that the isotopic composition of the carbonate being measured reflects that of the average, global surface ocean. This implies that the isotopic signal must be both primary (unaltered) and representative of contemporaneous, well-mixed ocean water. While quantitative studies have been done to demonstrate pathways in which carbonates and, specifically, $\delta^{13}C$ are susceptible to diagenetic alteration (Banner and Hanson, 1990; Allan and Matthews, 1982), few have focused on the processes which can result in the $\delta^{13}C$ values of ancient carbonate platforms to differ from the $\delta^{13}C$ composition of the ancient global ocean system (Immenhauser et al., 2002). These latter processes, which are oceanographic effects, are related to the convolution of geochemically distinct water masses of the open ocean and restricted epeiric seas.

  From studies of the modern ocean it is known that the $\delta^{13}C$ of seawater dissolved inorganic carbon (DIC) can vary significantly with oceanographic setting, with modern carbonate platforms being up to 4 per mil lighter than that of open ocean water (Patterson and Walter 1994). In general, it is the restricted circulation and long residence time of water in the platform setting which allows for the accumulation of ^{12}C-enriched carbon dioxide from oxidized organic matter. Although these oceanographic effects are expressed as lateral variations in $\delta^{13}C$, it has been postulated that they can be

recorded in stratigraphic profiles during the rise or fall of local sea-level (e.g. mixing of open ocean and restricted platform water masses, Holmden et al., 1998; Immenhauser et al., 2002; Immenhauser et al., 2003; Fanton and Holmden, 2007). Whereas positive shifts in δ^{13}C are often interpreted to reflect periods of increased burial of organic matter in sediments (global carbon cycle changes), the above references attempt to show that local and regional effects associated with sea-level changes can be the dominate processes affecting δ^{13}C. In order to test the hypothesis that δ^{13}C curves from carbonates deposited in epeiric seas record local oceanographic effects, I examined the relationships among δ^{13}C, δ^{18}O, and sea-level from two Ordovician stratigraphic sections during intervals with known transgressive-regressive sequences.

Geologic Setting

Sections for this study were sampled from Middle-Late Ordovician strata along I-35 in the Arbuckle Mountains of Oklahoma and along I-70 in the Appalachian Mountains near Clear Spring, Maryland. The Ordovician strata of the Arbuckle Mountains were deposited in a widespread epeiric seaway and sat adjacent to the Southern Oklahoma Aulacogen (Bambach et al., 1980) with facies ranging from the inner ramp to the outer ramp (Carlucci et al., 2012). The St. Paul Group and Chambersburg Formation of Maryland were deposited on a carbonate platform associated with the flexurally subsiding Appalachian foreland basin system, with the base of the St. Paul Group marking the Sauk-Tippecanoe megasequence boundary (Read, 1980; Brezinski et al., 2012).

Methods

The two sections utilized of the Middle to Upper Ordovician are correlated based on conodont index fossils (*C. sweeti* to *gerdae* zones) and appear to exhibit a contemporaneous, positive $\delta^{13}C$ trend. For $\delta^{13}C$ and $\delta^{18}O$ analyses, rock specimens were cut with a water-based, diamond-blade saw and sonicated in a water bath to expose fresh, unweathered surfaces. Fresh surfaces were microdrilled to produce a fine powder of matrix micrite with special care given to avoiding skeletal components and calcitic veins. A 75-95μg carbonate subsample was processed for each specimen in a Finnigan Delta Plus IV coupled with a Kiel III carbonate device stable isotope mass spectrometer, with standard deviations of repeated measurements from an internal standard of ± 0.03‰. Approximately 10% of all samples were run in duplicates with no significant variations. Although brachiopod shells are often considered the most reliable form of carbonate to conduct $\delta^{13}C$ analysis because of their resistance to diagenesis, these shells are not always sufficiently abundant to construct secular $\delta^{13}C$ trends. Matrix micrite is thus chosen because of its abundance and in order to test its robustness during changes in local sea-level, given that the use of matrix micrite for $\delta^{13}C$ analysis has become widespread (Saltzman et al., 1998; Payne et al., 2004; Saltzman and Young, 2005; Johnston et al. 2012). The sequence stratigraphic framework for this study of the Bromide Formation is from Carlucci et al. (2012), who worked at the same outcrop which was sampled for this study. For the St. Paul Group and Chambersburg Formation, sequence stratigraphy was also based on interpretations of lithostratigraphic relationships but within a more regional context by Brezinski et al. (2012).

Results

Carbon isotope curves from Ordovician strata of the Arbuckle Mountains, Oklahoma and Clear Spring, Maryland both reveal a long-term positive shift in $\delta^{13}C$ of approximately 3‰ magnitude beginning in the upper Darriwilian and continuing through the Sandbian. Sequence stratigraphy from the Bromide Formation in the Arbuckle Mountains indicates three third-order depositional sequences superimposed on a second-order, transgressive-regressive sequence (Carlucci et al., 2012). $\delta^{13}C$ from the Bromide exhibits a gradual, positive trend beginning at -3‰ and ending near 0‰ and is punctuated with two short negative shifts of ~1‰ magnitude (Fig. 2).

The St. Paul group and the Chambersburg Formation from Clear Spring display a third order, regressive-transgressive sequence, with transgression occurring just before the base of the Chambersburg Formation. $\delta^{13}C$ begins between 0‰ and 1‰, decreases to just above -4‰ near the end of the Darriwilian, and increases to just below 1‰ into the Mohawkian where the positive trend appears to continue. The increase in $\delta^{13}C$ from its minimum of -4‰ precedes the onset of transgression (Fig. 3). Cross plots of $\delta^{13}C$ versus $\delta^{18}O$ indicate no significant correlation at either locality (Fig. 4).

Discussion

Results of $\delta^{18}O$ from these sections reveals effects from diagenesis based on the generally scattered or invariant trends seen in both sections, as is often the case for bulk-rock sampling for $\delta^{18}O$ analysis. Consequently, $\delta^{18}O$ in bulk carbonate has little use for reconstructing temperature or paleoceanographic trends. However, because cross plots of $\delta^{13}C$ versus $\delta^{18}O$ reveal no correlation (Fig. 4), it appears that meteoric

diagenetic overprinting was not a significant process which altered δ^{13}C along with δ^{18}O. As a result, the focus of this discussion will be on δ^{13}C and its relationship to sea-level.

In order to assess the significance of local sea-level and water mass residence time on the carbon isotope record, I compared our stratigraphic trends of δ^{13}C with the interpreted sequence stratigraphy at both localities. The strata from the Arbuckle Mountains display a general positive trend in δ^{13}C with two punctuated negative δ^{13}C shifts. As seen in Fig. 2, the first portion of the section begins with a positive trend in δ^{13}C and is contained within a transgressive and a highstrand systems tract. This trend reverses at the first sequence boundary with a negative shift in δ^{13}C which coincides with another transgressive event. The negative shift continues into the highstand portion of the sequence where it inflects into a positive trend and continues as such through falling stand, lowstand, transgressive, and highstand systems tracts. From the St. Paul Group and Chambersburg formation of Clear Spring, there is a negative shift associated with regression, but an inflection toward a positive shift which precedes the onset of transgression (Fig. 3).

The overall relationship observed here between sequence stratigraphy and δ^{13}C at both localities suggest that sea-level fluctuations are not the dominant mechanism governing changes in δ^{13}C. In contrast to the ocean-mixing model proposed by Immenhauser et al. (2003), I do not consistently observe positive shifts associated with transgression or negative shifts associated with regression or lowstand tracts (Fig. 5). However, worth noting is that the negative shift seen in the Upper Darriwilian from Clear Spring is of greater magnitude than is documented elsewhere (Saltzman and Young, 2005; Ainsaar et al., 2010; Schmitz et al., 2010). I suggest the large magnitude can be attributed to seawater 'ageing' processes being superimposed on a global,

negative shift in $\delta^{13}C$. This 'ageing' process can occur during a period of restricted circulation which enables the accumulation CO_2 from oxidized organic matter enriched in ^{12}C (Holmden et al., 1998). This CO_2 will form bicarbonate ions where it can be incorporated into the skeletal material of carbonate-forming organisms and record the $\delta^{13}C$ of the locally altered sea-water.

The correspondence between the positive shift in $\delta^{13}C$ seen in Oklahoma, Maryland (this study) and in the Antelope Range, Nevada (Saltzman and Young, 2005) which are each associated with very different tectonic and regional settings implies that the shift is being driven by changes in the global carbon cycle as a result of increased rates of organic carbon burial. Although Patterson and Walter (1994) show that modern restricted platforms can become geochemically distinct from the open ocean due to local and regional processes, the difference in $\delta^{13}C$ largely depends on the proximity to the open ocean, with extreme cases like Florida Bay being close to a large volume of freshwater where inputs of weathered carbon are high (Fanton and Holmden, 2007). It is not likely that the carbonates from these sections were deposited in such extreme cases of restricted circulation, similar to that of the modern Florida Bay due to the presence of conodont microfossils throughout our sections. More likely, is a type of setting similar to the Bahama Banks where there is some, but limited exchange with the open ocean and the $\delta^{13}C$ of $\Sigma CO2$ can often be within 1‰ of that of open ocean water (see Patterson and Walter, 1994). The conclusions derived from Immenhauser and others (2002, 2003) which suggest a close coupling between $\delta^{13}C$ and sea-level are based on isotopic data from sections with limited controls for stratigraphic correlation (e.g. marker beds). As such, their study may potentially compare units of different time or with hiatuses which may affect the interpretations. If the observed positive shift seen

by Immenhauser and others (2002, 2003) is an artifact of switching to an open marine water mass with a different isotopic composition, one would not expect the trend to reverse unless the oceanographic setting also reversed due to regression and eventually a lowstand systems tract. Upon close inspection of the sequence stratigraphy following the positive shift in $\delta^{13}C$, it is not clear that there was a regressive event which could have caused the negative shift which follows the positive shift. This suggests that the shift may be related to changes in organic carbon burial.

Furthermore, if the interval studied by Immenhauser and others (2002, 2003) from the Pennsylvanian occurred during a period of favorable aragonite production, their observed shifts in $\delta^{13}C$ may be a result of an increased presence of ^{13}C-enriched aragonite sediments associated with sea-level rise, as described by Swart (2008). During the dominantly calcitic seas of the early Paleozoic (see Dickson, 2002 and references therein for a discussion of calcite-aragonite seas), it is unlikely that a shift to aragonite would occur and produce the major variations in $\delta^{13}C$ that are recorded in the Ordovician sections from this study. Additionally, in contrast to the findings of Fanton and Holmden (2007) which suggest that positive changes in $\delta^{13}C$ may be related to large-scale episodes of continental flooding, and, specifically, that sea-level changes result in $\delta^{13}C$ changes due to local C-cycle perturbations, I observe an overall positive trend in the Arbuckle Mountains during a high-order transgressive-regressive sequence in which a local increase in primary productivity is unlikely to account for the shift. Further, although Fanton and Holmden (2007) suggest their record of $\delta^{13}C$ during the Middle to Late Ordovician is closely related to changes in sea-level, the relationship between transgression and positive shifts in $\delta^{13}C$ or regression and negative shifts is complex (see time slices C1, C2, C4, C6 of their Fig. 3 where the coupling seems poor).

Conclusions and Implications

While I do not discount the presence of paleoceanographic effects on the isotope record, based on the results seen here, I suggest that these effects are negligible in certain circumstances. These Ordovician sections from Oklahoma and Maryland demonstrate poor coupling between changes in the local sea-level and changes in δ^{13}C. Although there may have been local effects such as sea-water 'ageing' processes on at least one part of our section at Clear Spring, Maryland, the δ^{13}C signal observed appears to be dominated by global changes in the carbon cycle. I postulate this based on the correlation of the trend from different regional and tectonic settings and the poor coupling between the shift and local sea-level. This positive shift in δ^{13}C, if due to increased organic carbon burial, may represent one of the first cooling events which led to the glaciations of the Late Ordovician (Saltzman and Young, 2005).

Recommendations for Future Work

It would be useful for this study to have detailed results of the sequence stratigraphy for the Middle-Upper Ordovician sections of the western United States for additional comparison purposes. It would also be useful to have more δ^{13}C data for this time interval from other continents outside of Laurentia and Baltica to test whether the positive shift seen is truly a global signal. Additionally, to further explore the question of to what degree can changes in sea-level affect the carbon isotope record, it would be interesting to model the timescale involved in δ^{13}C fluctuations which are a result of sea-level changes. For example, how long does it take for 'ageing' processes to become significant? How many moles of organic carbon would need to be oxidized to produce a +4‰ positive δ^{13}C shift? If high-amplitude flooding events do result in positive shifts

in $\delta^{13}C$, should this be recorded as an instantaneous change or can it be gradual? Or, how much flooding is necessary to flush the platform and mix open marine waters with the platform waters?

Acknowledgements

References

Ainsaar, L., Kaljo, D., Martma, T., Meidla, T., Männik, P., Nõlvak, J., and Tinn, O., 2010, Middle and Upper Ordovician carbon isotope chemostratigraphy in Baltoscandia: A correlation standard and clues to environmental history: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 294, no. 3–4, p. 189-201.

Allan, J., and Matthews, R., 1982, Isotope signatures associated with early meteoric diagenesis: Sedimentology, v. 29, no. 6, p. 797-817.

Bambach, K.R., Scotese, C.R., and Ziegler, A.M., 1980, Before Pangea: the geographies of the Paleozoic world: American Scientist, v. 68, p. 26-38.

Banner, J.L., and Hanson, G.N., 1990, Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis: Geochimica et Cosmochimica Acta, v. 54, no. 11, p. 3123-3137.

Blakey, R., 2008, Paleogeography and geologic evolution of North America. Retrieved from <http://www2.nau.edu/rcb7/namO450.jpg>

Brezinski, D.K., Taylor, J.F., and Repetski, J.E., 2012, Sequential development of platform to off-platform facies of the great American carbonate bank in the central Appalachians, *in* J.R. Derby, R.D. Fritz, S.A. Longacre, W.A. Morgan, and C.A. Sternback, eds., The great American carbonate bank: The geology and economic resources of the Cambrian-Ordovician Sauk megasequence of Laurentia: AAPG Memoir 98, p. 383-420.

Carlucci, J.R., 2012, Cyclicity and depositional sequences in a mixed siliciclastic – carbonate unit: Implications for intrabasinal correlation and subaqueous erosion in the Ordovician of Oklahoma: Geological Society of America Abstracts with Programs, v. 44, no. 7, p. 1222-1224.

Dickson, J., 2002, Fossil echinoderms as monitor of the Mg/Ca ratio of Phanerozoic oceans: Science, v. 298, no. 5596, p. 1222-1224.

Fanton, K., and Holmden, C., 2007, Sea-level forcing of carbon isotope excursions in epeiric seas: implications for chemostratigraphy: Canadian Journal of Earth Sciences, v. 44, p. 807-818.

Holmden, C., Creaser, R., Muehlenbachs, K., Leslie, S., and Bergström, S., 1998, Isotopic evidence for geochemical decoupling between ancient epeiric seas and bordering oceans: Implications for secular curves: Geology, v. 26, no. 6, p. 567-570.

Immenhauser, A., Kenter, J.A., Ganssen, G., Bahamonde, J.R., Van Vliet, A., and Saher, M.H., 2002, Origin and significance of isotope shifts in Pennsylvanian carbonates (Asturias, NW Spain): Journal of Sedimentary Research, v. 72, no. 1, p. 82-94.

Immenhauser, A., Della Porta, G., Kenter, J.A.M., and Bahamonde, J.R., 2003, An alternative model for positive shifts in shallow-marine carbonate $\delta^{13}C$ and $\delta^{18}O$: Sedimentology, v. 50, no. 5, p. 953-959.

Johnston, D., Macdonald, F., Gill, B., Hoffman, P., and Schrag, D., 2012, Uncovering the Neoproterozoic carbon cycle: Nature, v. 483, no. 7389, p. 320-323.

Patterson, W.P., and Walter, L.M., 1994, Depletion of ^{13}C in seawater ΣCO_2 on modern carbonate platforms: Significance for the carbon isotopic record of carbonates: Geology, v. 22, no. 10, p. 885-888.

Payne, J.L., Lehrmann, D.J., Wei, J., Orchard, M.J., Schrag, D.P., and Knoll, A.H., 2004, Large perturbations of the carbon cycle during recovery from the end-Permian extinction: Science, v. 305, no. 5683, p. 506-509.

Read, J., 1980, Carbonate ramp-to-basin transitions and foreland basin evolution, Middle Ordovician, Virginia Appalachians: AAPG Bulletin, v. 64, no. 10, p. 1575-1612.

Saltzman, M.R., Runnegar, B., and Lohmann, K.C., 1998, Carbon isotope stratigraphy of Upper Cambrian (Steptoean Stage) sequences of the eastern Great Basin: Record of a global oceanographic event: Geological Society of America Bulletin, v. 110, no. 3, p. 285-297.

Saltzman, M.R., and Young, S.A., 2005, Long-lived glaciation in the Late Ordovician? Isotopic and sequence-stratigraphic evidence from western Laurentia.: Geology, v. 33, no. 2, p. 109-112.

Schmitz, B., Bergström, S.M., and Xiaofeng, W., 2010, The middle Darriwilian (Ordovician) $\delta^{13}C$ excursion (MDICE) discovered in the Yangtze Platform succession in China: implications of its first recorded occurrences outside Baltoscandia: Journal of the Geological Society, v. 167, no. 2, p. 249-259.

Swart, P.K., 2008, Global synchronous changes in the carbon isotopic composition of carbonate sediments unrelated to changes in the global carbon cycle: Proceedings of the National Academy of Sciences, v. 105, no. 37, p. 13741-13745.

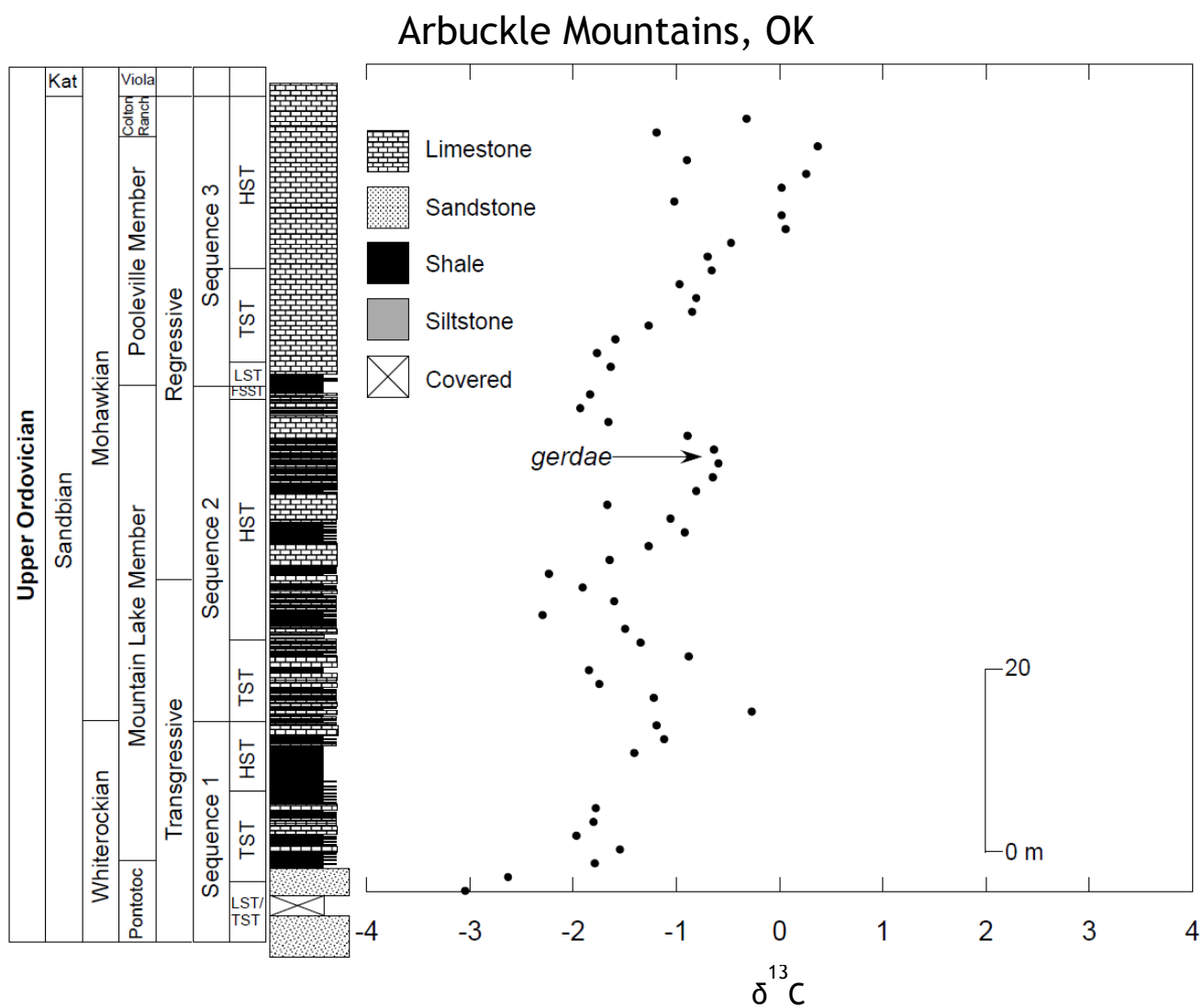**Fig. 1.** Paleographic map of the Late Ordovician, approximately 450Ma. Credit: Ron Blakey (2008).

Fig. 2. Stratigraphic plots of δ^{13}C from the Arbuckle Mountains, OK. Lithologies and sequence stratigraphy taken from Carlucci et al., (2012).
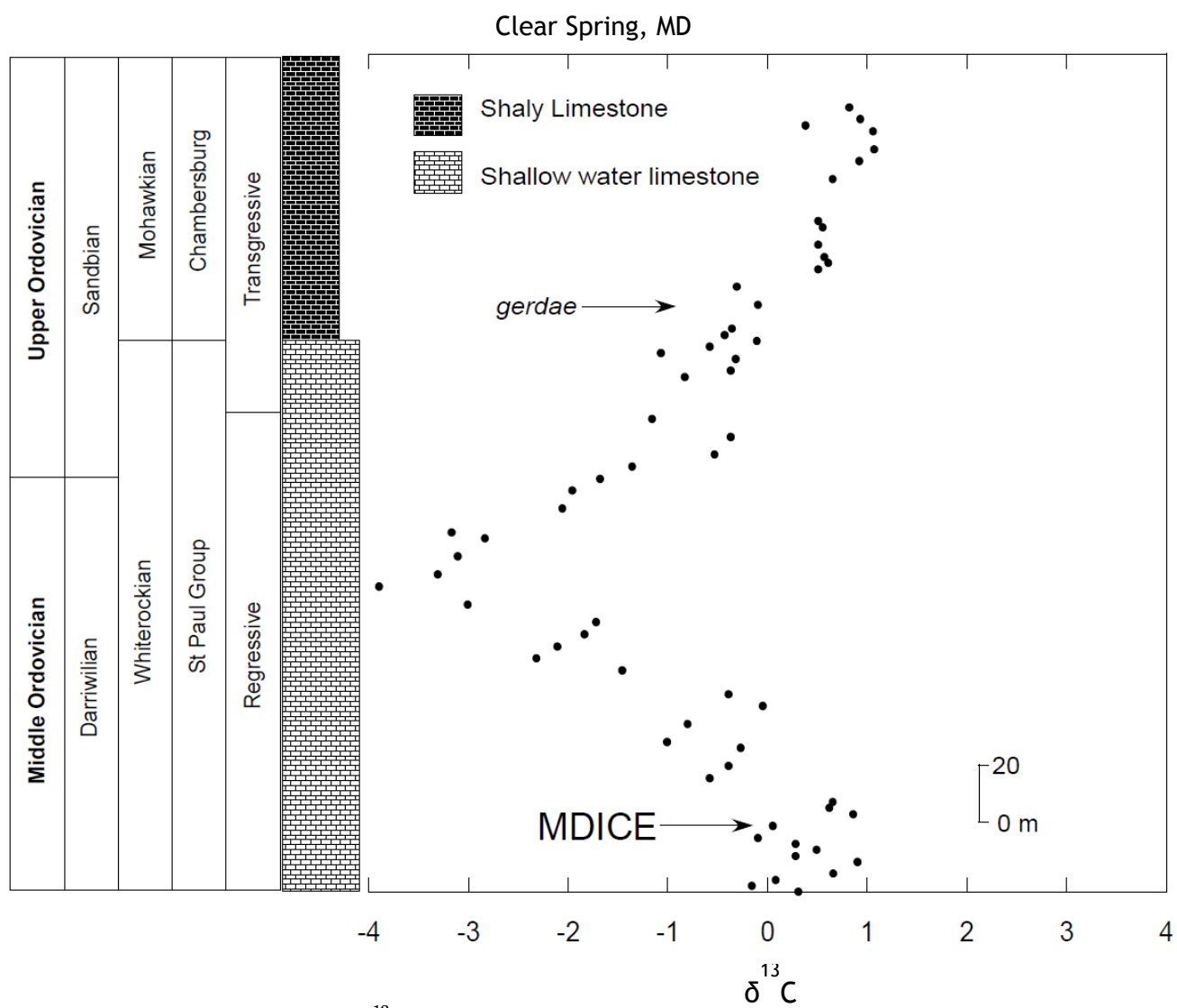
Fig. 3. Stratigraphic plot of δ¹³C from the Clear Spring, MD, sequence stratigraphy taken from Brezinski et al. (2012).
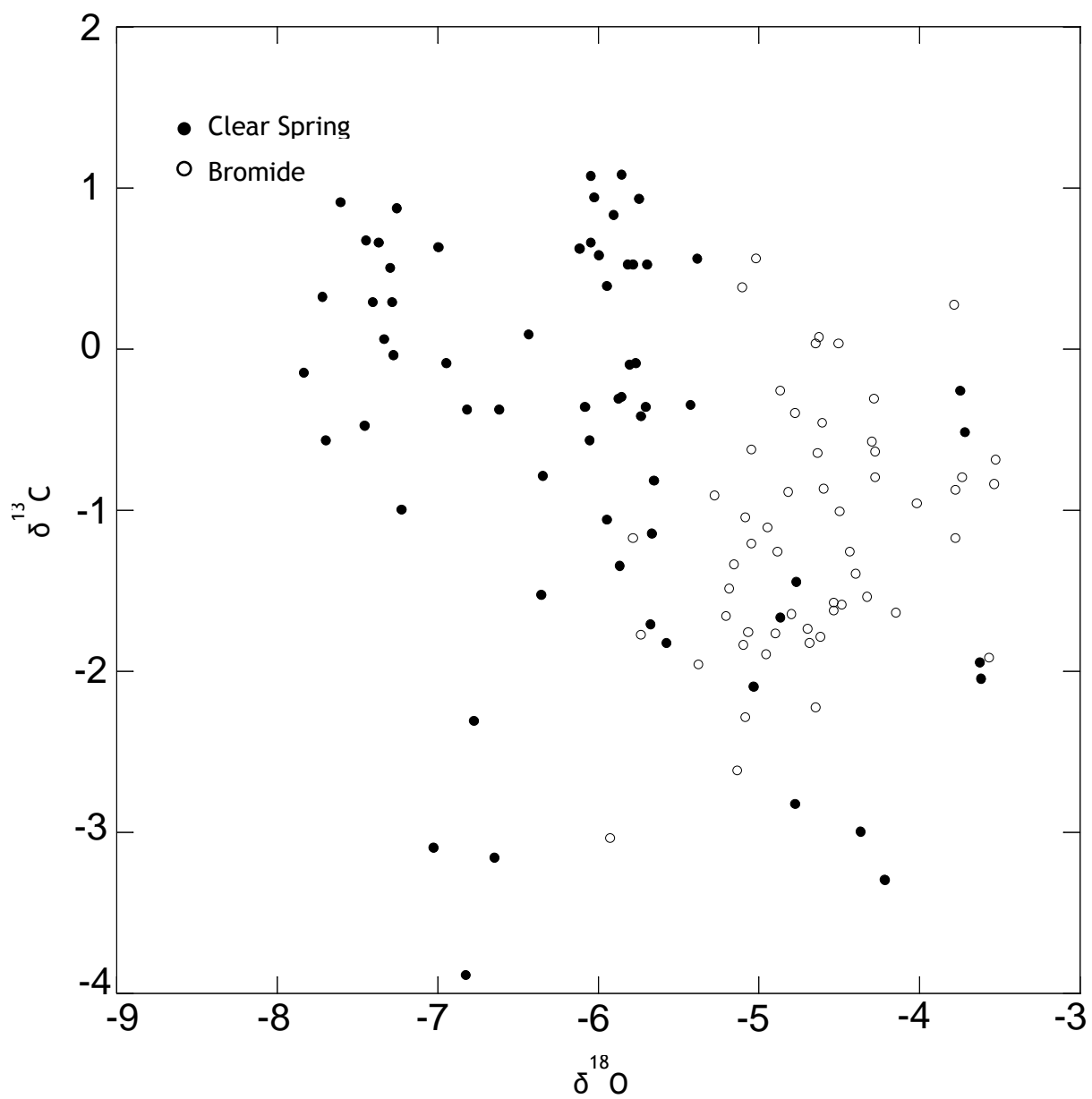
Fig. 4. Cross plot of $\delta^{13}C$ versus $\delta^{18}O$.

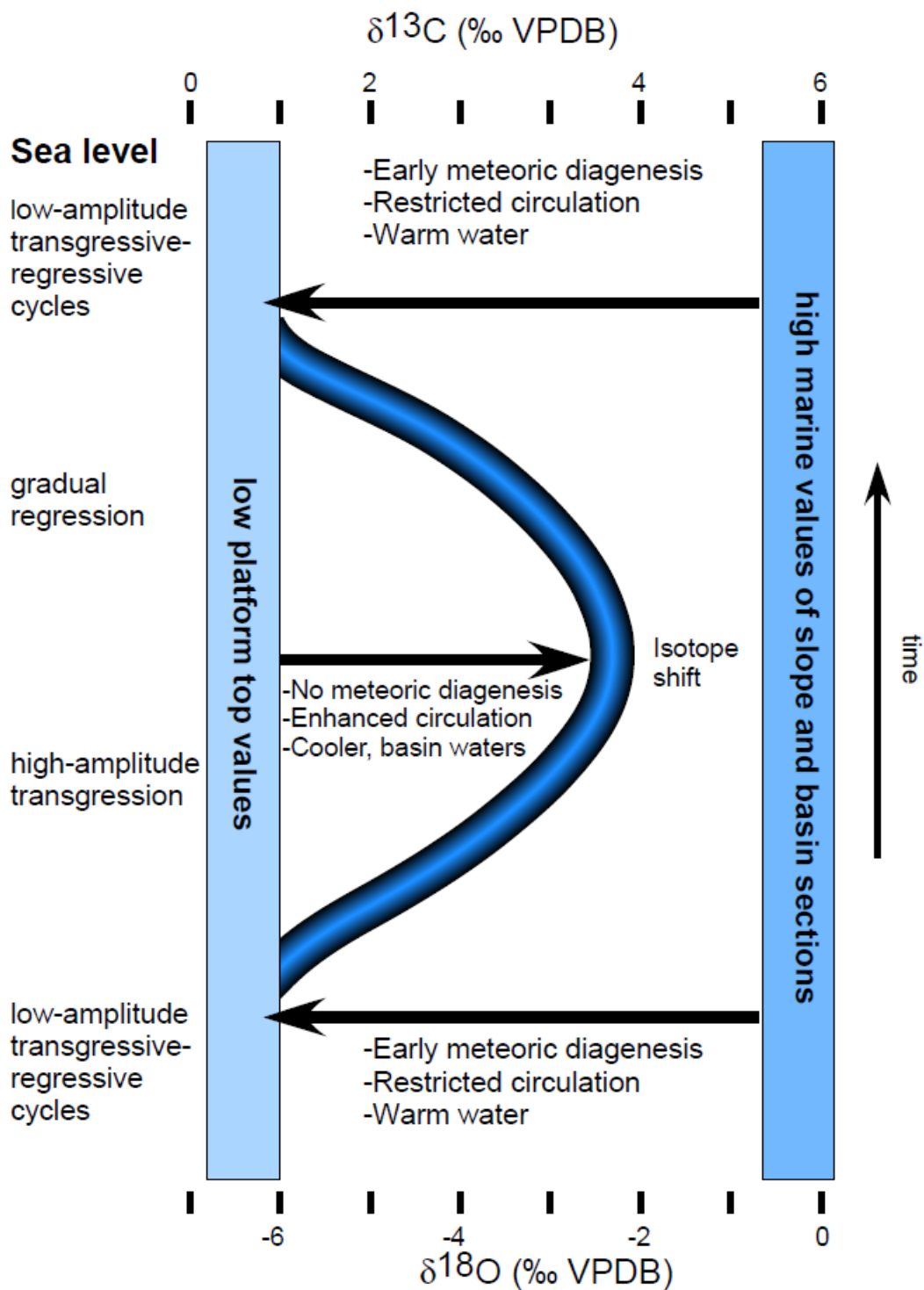**Fig. 5.** Alternative model for explaining isotope shifts of δ¹³C and δ¹⁸O. Figure modified from Immenhauser et al., (2003).